Simulation Study of Ammonia Synthesis Loop Reactor-Separator System

by

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(12215)

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CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. Lemma Dendena Tufa)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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TENGKU MOHD HILMI BIN TENGKU ZAINAL ALAM SHAH

ABSTRACT

The Ammonia recovery is not extremely efficient so the recycled gas typically contains 4.0% mol fraction of Ammonia (Appl.M,2003). Some specific energy is consumed just to recycle small amount of Ammonia back to the Reactor. Thus, the objectives of the project is to simulate and study the Ammonia synthesis loop using iCON® Process Simulation software as well as to investigate the best operating conditions of Ammonia Reactor-Separator System in order to minimize the fraction of unrecovered Ammonia in the recycled gas. The scope of this work focuses on the synthesis and development of the flowsheet for the Ammonia synthesis loop process in PETRONAS's iCON® Process Simulation software. The simulated Ammonia synthesis is achieved in Ammonia Reactor at temperature of 250 ^{o}C and pressure of 135 atm with 25% reaction conversion. From the simulation, about 6.5% mol fraction of Ammonia is predicted in the recycled gas. The effects of inlet temperature and pressure of Ammonia Reactor-Separator towards the amount of unrecovered Ammonia in the recycled gas were studied. Based on the result, minimum fraction of unrecovered Ammonia in the recycled gas favored at low temperature and high pressure at the inlet stream of Ammonia Separator. The best operating conditions for the inlet stream of Ammonia Separator is deduced at -5.0 ^{o}C and 140 kg.f/cm^{2} respectively. Meanwhile changing the inlet temperature and pressure of Ammonia Reactor does not give significant changes on the fraction of unrecovered Ammonia in the recycled gas. Comparisons of the simulation result are also made with the real plant data from literature.

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The past 28 weeks of my enrolment in Final Year Project have been truly valuable experience to me. I have learned many aspects and knowledge from my Final Year Project on the Ammonia Synthesis Loop unit. I have broadened my knowledge and experiences in these related fields. Hence, I would like to take this opportunity to express my sincerest gratitude to a number of people that have helped me to achieve this.

First of all I would like to express my gratitude to God for letting me to complete this project in good health and well-being. Next, I would like to express my deepest appreciation to Dr. Lemma Dendena Tufa, my FYP supervisor, who has supervised me throughout my project period. His ever willingness to teach me and guide me has helped me on my Final Year Project.

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ABBREVIATIONS AND NOMENCLATURES

N_2 Nitrogen

H_2 Hydrogen

NH_3 Ammonia

Ar Argon

CH_4 Methane

η Efficiency

ΔP Pressure Drop

x_{NH_3} Ammonia mol fraction

kg.f/cm^2 kilogram force per squared centimeter

N m^3/h Normal m^3/h (0 ^{o}C,760 mmHg)

CHAPTER 1
INTRODUCTION

1.1 Background of Study

After sulphuric acid, Ammonia is the second largest common chemical worldwide. It is used in production of chemical fertilizers, explosive materials, polymers, acids and even coolers. In Ammonia production, Hydrogen and Nitrogen are reacted at high pressure to form Ammonia. Ammonia synthesis occurs via the following reversible exothermic chemical reaction: $N_2 + 3H_2 \leftrightarrows 2NH_3$ and is typically performed over promoted iron, Fe catalysts in catalytic converters at pressures ranging from 150-250 atm at a minimum temperature of 300-550°C. Therefore, Ammonia synthesis takes place at high temperatures and pressures and with a substantial recycle. Several basic processing activities are required by the Ammonia Synthesis Loop in order to convert the Hydrogen and Nitrogen to Ammonia product.

During the reaction, Ammonia is recovered from the synthesis loop by cooling the synthesis gas at process pressures to condense the Ammonia. But per-pass conversion through an Ammonia synthesis reaction is low (10-35%) and is limited by equilibrium. The liquid Ammonia is separated from the gas, which is recycled back through the reactor. Earlier plant designs used air or water-cooling for Ammonia recovery. Modern synthesis plants use refrigeration to condense out the Ammonia (Appl.M,2003).

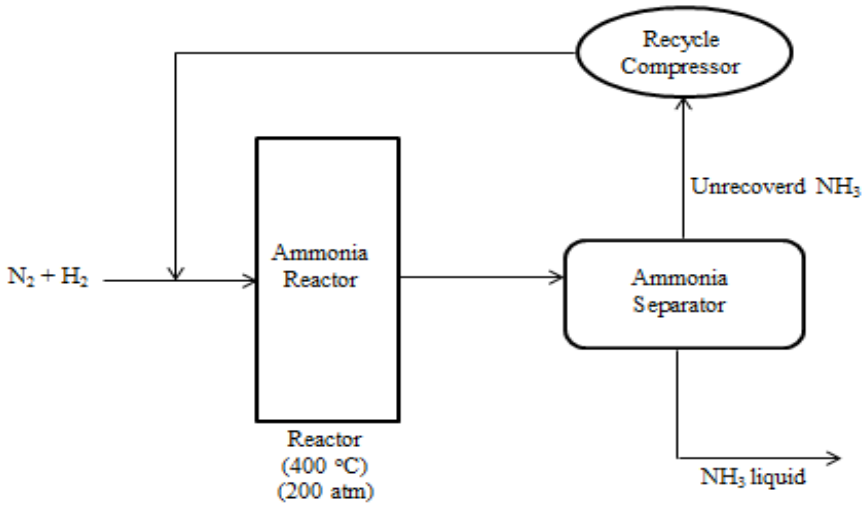


Figure 1.1 Ammonia Synthesis Loop

Although its synthesis is an exothermic reaction, obtaining the raw-materials is an energy consuming step, especially for Hydrogen, if water is use as resource. Since the conversion per pass is not 100%, the reactor is operated in loop mode. Ammonia is continuously condensed out of the loop and fresh synthesis gas is added. Because the synthesis gas contains small quantities of Methane and Argon, these impurities build up in the loop and must be continuously purged to prevent them from exceeding a certain concentration.

Purging some of the gas in the recycle loop before it is recycled minimizes inert gas concentrations (Appl.M,2003). In addition, this purged gas contains some product Ammonia that is recovered, unconverted Nitrogen and Hydrogen, plus the inert gases. The purged Hydrogen is recovered and recycled back to the reactor or used as a fuel in the process. Some of the inert gases also end up dissolved in the condensed Ammonia product. Flashing the liquid Ammonia in a pressure letdown step releases any dissolved gases that are separated from the product. Although this purge stream can be used to supplement reformer fuel gas, it contains valuable Hydrogen which is lost from the Ammonia synthesis loop.

Hence, Ammonia synthesis loop is the most important part for this project which require the depth understanding of iCON® Process Simulation software to study the composition of unrecovered Ammonia in the recycling stream. Morever, the iCON® process simulation software that used in this project is used to investigate the best operating conditions of Ammonia Reactor-Separator in order to minimize the composition of unrecovered Ammonia in the recycled gas after completed the simulated of Ammonia Synthesis.

1.2 Problem Statement

In the synthesis of Ammonia, small amount of unrecovered Ammonia is present in the recycled gas where a specific energy of Ammonia is required to recycle it back to the reactor. In addition, increasing amount of unrecovered Ammonia in the recycled gas will make the equilibrium conversion to shift towards the backward reaction to produce more Hydrogen and Nitrogen instead of producing more Ammonia product as explained by Le' Chatelier's principle. Hence, minimizing as much as composition of unrecovered Ammonia in the recycled gas will save some energy that used just to recycle back the unrecovered Ammonia and subsequently will favor the forward reaction in producing more Ammonia. Thus, it is required to investigate the best operating conditions (Temperature and Pressure) in the Ammonia Reactor-Separator in order to minimize the amount of unrecovered Ammonia in the recycled gas.

1.3 Objectives and Scope of Study

There are **TWO (2)** main objectives highlighted for this project as stated below:

- To simulate and study the Ammonia synthesis loop using iCON® Process Simulation software.
- To investigate the best operating conditions of Ammonia Reactor-Separator system to minimize the fraction of unrecovered Ammonia in the recycled gas.

Meanwhile, the scope of sudy for this project is mainly to model the Ammonia synthesis loop which based on the real data obtained from the literature review. This simulation model would be done using the iCON® Process Simulation software. The study will be divided into two main parts where by the first phase involves researching on this project. These researching are done based on the limited journals available online and academic books that had been read and recommended. Meanwhile, the second phase of this project is to simulate the Ammonia synthesis loop model using iCON® Process Simulation software. Hence, this project would requires in-depth understanding on the iCON® Process Simulation software.

1.4 The Relevancy and Feasibility of the Project

This project is relevant to the author's field of study since simulation and modelling an Ammonia Synthesis loop is one of the focus area in Chemical Engineering. The Ammonia Synthesis loop is a major process in a Ammonia plant which involves a lot of Chemical Engineers in building and maintaining it. Study of the composition of the unrecovered Ammonia in the recycled gas is important in order to minimize the energy required to recycle the Ammonia back to the Reactor and at the same time to maximize the production of Ammonia. In addition, simulation of Ammonia synthesis loop is one of the many skills that a Chemical Engineer is exposed to based on the knowledge of mass and energy balance and thermodynamics.

In the same time, this project also is feasible since it is within the scope and time frame. The author has planned to complete the research and literature review by the end of the first semester (May 2012) while the author was doing some tutorials and get to know the iCON® Process Simulation software well. In the second semester (September 2012), the author has planned to dedicate the first seven weeks to input the real field data from the literature review into the iCON® Process Simulation software. Then, the author would analyzed the result achieved in the iCON® software to solve the objectives that had been stated in this project

CHAPTER 2

LITERATURE REVIEW

2.1 Fundamentals of the Ammonia Synthesis Reaction

To fix a kilogram of Nitrogen in Ammonia requires reacting 2.4 m^3 (STP) of Hydrogen and 0.8 m^3 (STP) of Nitrogen where about 3.27 MJ of heat is evolved (Appl.M, 2003). Ammonia synthesis proceeds according to the following reaction;

$$0.5\ N_2 + 1.5\ H_2 \leftrightarrows NH_3; \qquad \Delta H_{298} = -46.22\ kJ/mol$$

Table 2.1(i) Thermodynamic data of Ammonia rxn at atm pressure (Appl.M,2003)

	Temperature,K							
	300	400	500	600	700	800	900	1000
ΔH, kJ	-46.35	-48.48	-50.58	-52.04	-53.26	-54.28	-55.06	-55.68
ΔS, J/K	-99.35	-105.63	-110.03	-112.71	-114.55	-115.89	-116.77	-117.48
ΔG/T, J/K	-55.22	-15.66	8.88	26.25	38.48	48.02	55.56	61.81
$C_{p,NH3,}$ J $mol^{-1}K^{-1}$	35.52	38,80	41.97	45.04	47.98	50.80	53.49	56.03
$C_{p,NH3,}$ J $mol^{-1}K^{-1}$	28.868	29.199	29.278	29.341	29.454	29.634	29.89	30.216
$C_{p,NH3,}$ J $mol^{-1}K^{-1}$	29.144	29.270	29.601	30.132	30.777	31.451	32.117	32.724

Table 2.1(ii) Heat of solution of Ammonia in water, in kJ/mol NH_3 (Appl.M,2003)

t, ^oC	Mixture ratio (moles of water per mole Ammonia)						
	1	2.33	4	9	19	49	99
0	30.69	34.25	35.17	35.80	36.22	36.47	36.09
20	27.38	32.87	33.66	34.50	34.67	34.83	34.92
40	24.53	31.99	32.91	33.62	33.87	33.95	34

2.1.1 Chemical Equilibrium

The reaction equilibrium of Ammonia synthesis has been investigated experimentally and theoritically many times. The values for the equilibrium constant are available for pressure up to 350 Mpa. Gillespie and Beattie (1930) were by the far the most successful experimentally in establishing a firm basis for an analytical expression of the equilibrium constant in the range of industrial interest. The values in **Tables 2.1.1(i)** and **2.1.1(ii)** below were calculated using their equation.

Table 2.1.1(i) Ammonia content (in mol%) in equilibrium synthesis gas (Gillespie and Beattie,1930)

t, ^{o}C	P_{abs}, MPa										
	5	10	20	30	40	50	60	70	80	90	100
300	39.38	52.79	66.43	74.20	79.49	83.38	86.37	88.72	90.61	92.14	93.39
400	15.23	25.15	38.53	47.86	55.06	60.91	65.81	69.99	73.59	76.71	79.43
500	5.56	10.39	18.61	25.54	31.60	37.02	41.94	46.46	50.62	54.48	58.06
600	2.28	4.48	8.69	12.69	16.52	20.20	23.76	27.22	30.57	33.83	37.00

Table 2.1.1(ii) Equilibrium Ammonia content (in mol %) in the presence of inert gases (Gillespie and Beattie,1930)

t, ^{o}C	P_{abs}, MPa										
	5	10	20	30	40	50	60	70	80	90	100
300	32.11	43.10	54.27	60.62	64.95	68.12	70.56	72.49	74.03	75.28	76.31
400	12.39	20.50	31.48	39.13	45.02	49.81	53.81	57.21	60.14	62.68	64.89
500	4.51	8.46	15.19	20.89	25.87	30.33	34.37	38.08	41.49	44.64	47.56
600	1.85	3.64	7.08	10.37	13.52	16.56	19.50	22.35	25.12	27.81	30.43

Figures 2.1.1 below show the effect of temperature and pressure on the equilibrium mole fraction of Ammonia. It can be seen that the Ammonia mole fraction decreases as the temperature is increased while it increase a the pressure is increased (Modak M.J,2002).

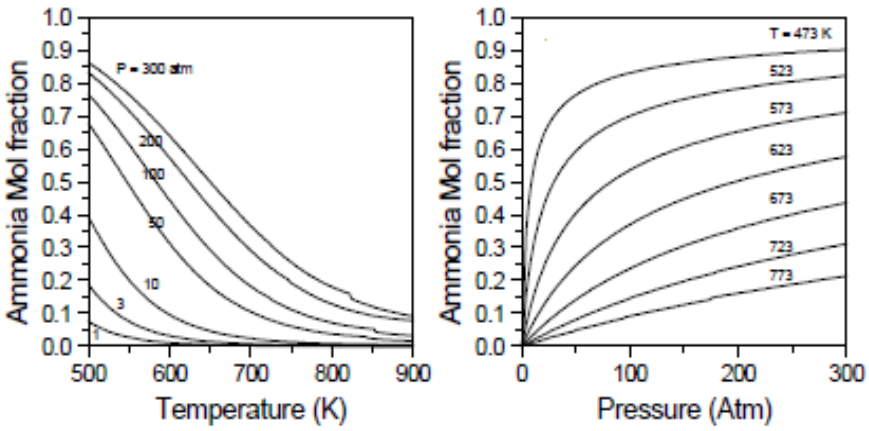


Figure 2.1.1 Temperature and pressure on the NH_3 mole fraction at equilibrium (Modak M.J,2002)

It can conclude then that Ammonia synthesis as per equation is an equilibrium reaction that is favoured by low temperature and high pressure. Equilibrium conditions is only a part of the picture, that is, thermodynamics does not give any idea about the rate of the reaction plus the reaction does not proceed at ambient temperature because Nitrogen requires a lot of energy dissociate (Modak M.J,2002).

2.1.2 Heat of Reaction

According to Appl.M (2003)

> Usually, a system having an exothermic heat of reaction under operating conditions should react spontaneously. However, to form Ammonia from Hydrogen and Nitrogen molecules, significant energy input is required for the Nitrogen molecule to achieve the activated state. This is because of its high dissociation energy of 941 kJ/mol, which is considerably higher than that of Hydrogen.(p.27)

Haber (1915) investigated the heat of reaction of Ammonia Synthesis at atmospheric pressure. Today, most people use the Gillespie-Beattie equation. This equation was used in calculating the values in **Table 2.1.2** below:

Table 2.1.2 Heat of reaction,ΔH (in kJ) of Ammonia Synthesis (Gillespie-Beattie,1930)

t, ^{o}C	P_{abs}, MPa									
	0	10	20	30	40	50	60	70	80	90
0	44.39	55.20	66.02	76.84	87.66	98.47	109.29	120.11	130.92	141.74
25	44.92	53.48	62.03	70.59	79.15	87.70	96.26	104.82	113.38	121.93
50	45.44	52.37	59.30	66.23	73.16	80.09	87.02	93.95	100.88	107.80
75	45.96	51.69	57.41	63.14	68.86	74.58	80.31	86.03	91.76	97.48
100	46.47	51.28	56.10	60.91	65.72	70.53	75.34	80.16	84.97	89.78
200	48.42	51.17	53.92	56.68	59.43	62.18	64.93	67.69	70.44	73.19
300	50.18	52.02	53.86	55.70	57.54	59.38	61.22	63.06	64.90	66.74
400	51.73	53.09	54.46	55.82	57.18	58.55	59.91	61.28	62.64	64.00
500	53.01	54.09	55.18	56.26	57.35	58.43	59.52	60.60	61.69	62.78
600	53.98	54.88	55.79	56.70	57.61	58.52	59.43	60.34	61.24	62.15

Meanwhile According to W.G Frankenburger (1955)

> According to estimates, the homogenous reaction of Nitrogen with Hydrogen to form Ammonia in the gas phase requires an activation energy of 230 – 420 kJ/mol. For purely thermal energy supply with a favorable collision yield, this activation barrier requires temperatures well above 800 – 1200 K to achieve measurable reaction rates. However, at such high temperatures and industrially reasonable pressures, the theoritically achievable ammonia yield is extremely small because of the unfavorable position of the thermodynamic equilibrium. In fact, all older attempts to combine molecular Nitrogen purely thermally with atomic or molecular Hydrogen failed. On the other hand, both Ammonia and hydrazine result from reacting atomic Nitrogen with atomic Hydrogen.(p.28)

R.Brill et al (1999) says that at pressures above 200 MPa, the synthesis of Ammonia proceeds even in the absence of specific catalyts. At such extreme pressures the vessel walls appear to catalyze the formation of Ammonia. In the catalytic combination of Nitrogen and Hydrogen, the molecules lose their translational degrees of freedom by fixation on the catalyst surface. This drastically reduces the required energy of activation, for example, to 103 kJ/mol on iron. The reaction may then proceed in the temperature range 250 - 400 ^{o}C.

2.1.3 Effect of Pressure, Temperature and H_2:N_2 ratio

According to G. R Maxwell (2004), high pressure promotes a high rate of Ammonia formation. From the **Figure 2.1.3(i)** below, it can be seen at ratio of 3:1 of Hydrogen to Nitrogen, higher pressure will give higher reaction rate. Thus, sufficiently high pressure would give better reaction rate. However, higher pressure would result to higher operating cost due to the duty of the compressor. Thus, an optimum pressure must be chosen.

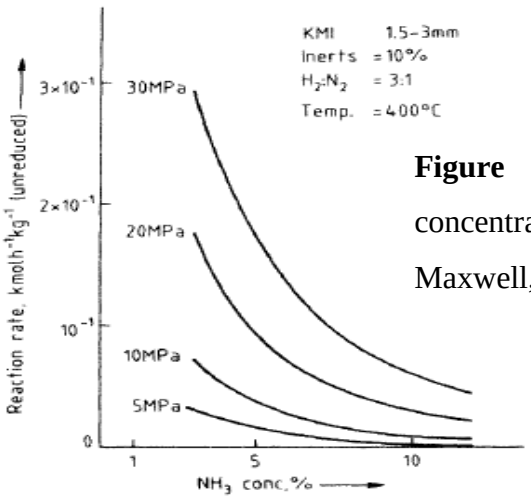


Figure 2.1.3(i) Reaction rate on NH3 concentration at various pressures (G.R Maxwell,2004)

Again, referring to G. R Maxwell (2004) the rate of formation initially increases with rising temperature but then goes through a maximum as the system approaches thermodynamic equilibrium as shown by **Figure 2.1.3(ii)** below. From here, it can be seen there is a limit to increase the temperature so that the reaction rate will be sufficiently high for the process. However, too low temperature will lower the rate of reaction. Hence, the temperature must be optimized in order to get better rate of reaction.

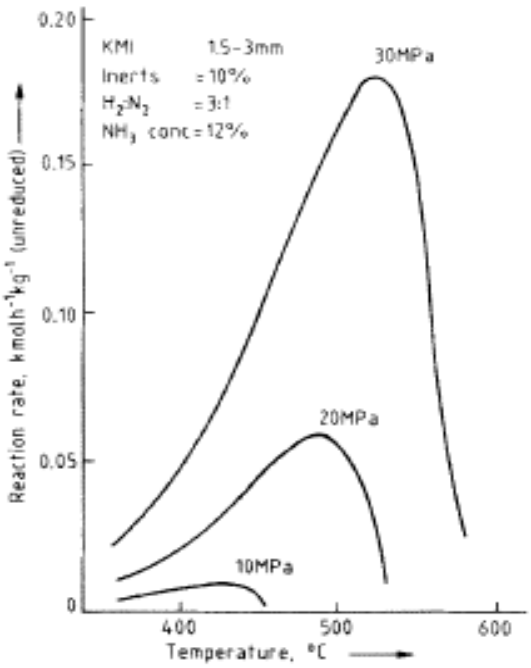


Figure 2.1.3(ii) Reaction rate at various temperatures of NH_3 synthesis (G.R. Maxwell,2004)

The **Figure 2.1.3(iii)** below shows that Ammonia synthesis rate constant is dependent on H_2: N_2 ratio. It can be seen that for 1:1 ratio, at lower temperature the rate constant is much higher however at higher temperature the rate constant decreases. It is known that, for the Ammonia production process, the temperature must be sufficiently high so that the rate of reaction will be higher. Meanwhile, for 3:1 ratio, it can be seen that the rate of reaction increases as the temperature increases. Hence, it can be concluded that 3:1 Hydrogen-Nitrogen ratio better for Ammonia production process.

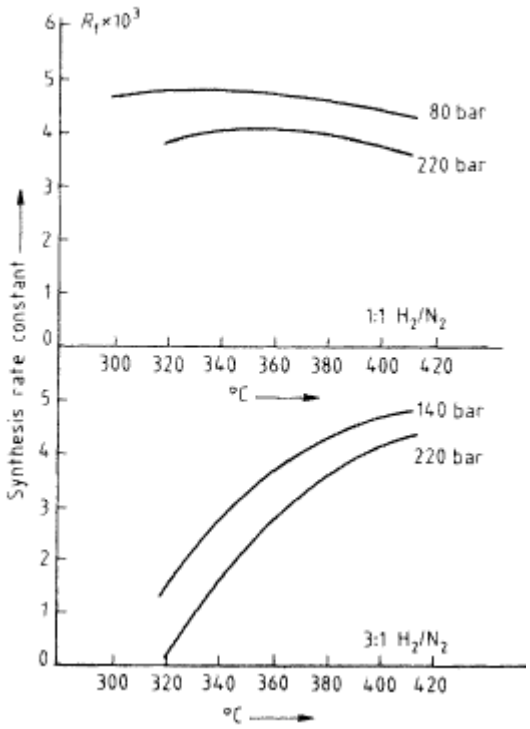


Figure 2.1.3(iii) Rate constant on H_2-N_2 ratio (Appl.M,2003)

In addition, equations for describing Ammonia synthesis under industrial operating conditions must represent the influence of the temperature, the pressure, the gas composition, and the equilibrium composition. Morever, they must also take into consideration the dependence of the Ammonia formation rate on the concentration of catalysts poisons and the influence of mass-transfer resistances, which are significant in industrial ammonia synthesis (Appl.M,2003).

2.1.4 Le' Chatelier's principle on Ammonia Synthesis

The formation of Ammonia is an exothermic reaction with considerable release of heat. The reaction is reversible reaction, that is, it can procees both in forward direction (Ammonia synthesis) and backward direction (Ammonia decomposition).

$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

The reaction is accompanied by decrease in volume because there is a decrease in number moles of gas from 2 to 1 (Modak M.J,2002).

By Le' Chatelier's principle on Ammonia synthesis:

- Increasing the pressure causes the equilibrium to shift to the right resulting in a higher yield of Ammonia since there is a pressure drop accompanying the transformation;
- Decreasing the temperature also cause the equilibrium position to move to the right again resulting in a higher yield of Ammonia since the reaction is exothermic (release heat).

2.2 Synthesis of Ammonia

Under the conditions practical from an industrial process, Ammonia formation from Hydrogen and Nitrogen;

$$N_2 + 3H_2 \leftrightarrows 2NH_3; \qquad \Delta H = -92.44 \text{ kJ/mol} \qquad \text{(Appl,2003)}$$

The process is limited by the unfavorable position of the thermodynamic equilibrium, so that only partial conversion of the synthesis gas (25-35%) can be attained on its passage through the catalyst (Appl.M,2003).

According to Appl.M (2003)

> Ammonia is separated from the unreacted gas by condensation, which requires relatively low temperatures for reasonable efficiency. The unconverted gas is supplemented with fresh synthesis gas and recycled to the converter. The concentration of the inert gases (CH_4 and Ar) in the synthesis loop is controlled by withdrawing a small continuous purge gas stream. These basic features together with the properties of the synthesis catalyst and mechanical restrictions govern the design of the Ammonia synthesis converter and the layout of the synthesis loop. Evaluation criteria are energy consumption, investment and reliability.

The central part of the Ammonia synthesis system is the converter, in which the conversion of the synthesis gas to Ammonia takes place. Converter performance is determined by the reaction rate, which depends on the operating variables. A number of Ammonia converters are commercially available. Seventeen different designs for Ammonia converters are described by Zardi (Zardi,1982). The article in Ullmanns's also contains figures and descriptions of several different Ammonia converters (Appl, 2003). Many designs are based on quench converters that have multiple catalyst beds in series and cold gas is introduced between the beds for temperature control.

In addition, the following rate expression for Ammonia synthesis was developed by Temkin and Pyzhev in 1940 and has been widely applied to Ammonia converter design and development (Jennings and Ward,1989),

$$r = k_1 P_{N_2} \left(\frac{P_{H_2}^{\ 3}}{P_{NH_3}^{\ 2}} \right)^{\alpha} - k_2 \left(\frac{P_{NH_3}^{\ 2}}{P_{H_2}^{\ 3}} \right)^{\beta} \quad \alpha + \beta = 1 \qquad \alpha, \beta > 0 \quad \text{(Temkin and Pyzhev,1940)}$$

where the first term is the rate of Ammonia formation and the second term is the rate of Ammonia decomposition. This rate expression is valid over a very wide pressure range with fugacities substituted for pressures at very high pressure. The value for α ranges between 0.4-0.75 for commercial processes where Ammonia is recycled back to the reactor. Clearly, this expression is not valid for zero Ammonia concentrations that are often encountered in the laboratory. For process using only pure reactants without Ammonia recycle, the following rate equation applies:

$$r = kP^{\alpha}{}_{(H_2)} P^{1-\alpha}{}_{(N_2)}$$

2.2.1 Ammonia Refrigeration Unit

Figure 2.2.1 below shows the Ammonia recovery unit processed by Karnafulli Fertilizer Company, KAFCO (2004). In Ammonia refrigeration unit, there are eight heat exchangers. Ammonia comes out from the converter at about 440 ^{o}C that passes through the eight heat exchangers to lower down the temperature up to the boiling point of NH_3 (-33) at atmospheric pressure. Heat is first exchanged in the waste heat boiler and then in the BFW preheater. There are cooler where cold water is used as a cooling agent. Two chillers are used to lower the temperature less that the ambient temperature. Ammonia is used as a refrigerating agent in the chillers. The NH_3 separator is used since some H_2 and other gases may be entrapped and the CH_4 and N_2, H_2 are removed for product purification so that in the letdown vessel flushing occurs.

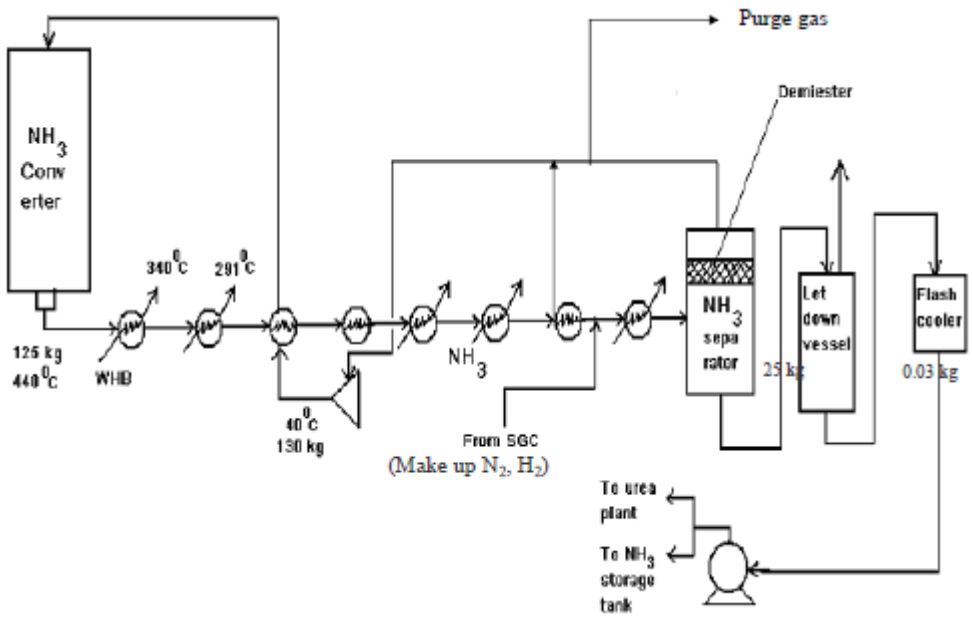


Figure 2.2.1 Ammonia Refrigeration unit (KAFCO,2004)

2.2.2 Ammonia Synthesis Loop by Krupp-Uhde

Figure 2.2.2 below is an example of modern Ammonia synthesis loop (Krupp – Uhde) with a two-vessel converter system and three indirectly cooled catalyst bed producing 1500 t/d NH_3 at 188 bar. The gas enters the converter (a) at 295 ^oC and is subsequently heated in the internal heat exchanger to 390 ^oC before it enters the first catalyst layer. The outlet gas from the first layer then passes through the aforementioned heat exchanger and enters the second bed, after which the gas leaves the converter with 469 ^oC and passes a waste heat boiler generating 125 bar steam. The inlet gas of the second vessel, which accomodates the third catalyst bed, has a temperature of 401 ^oC and the outlet enters a further waste heat boiler generating 125 bar steam.

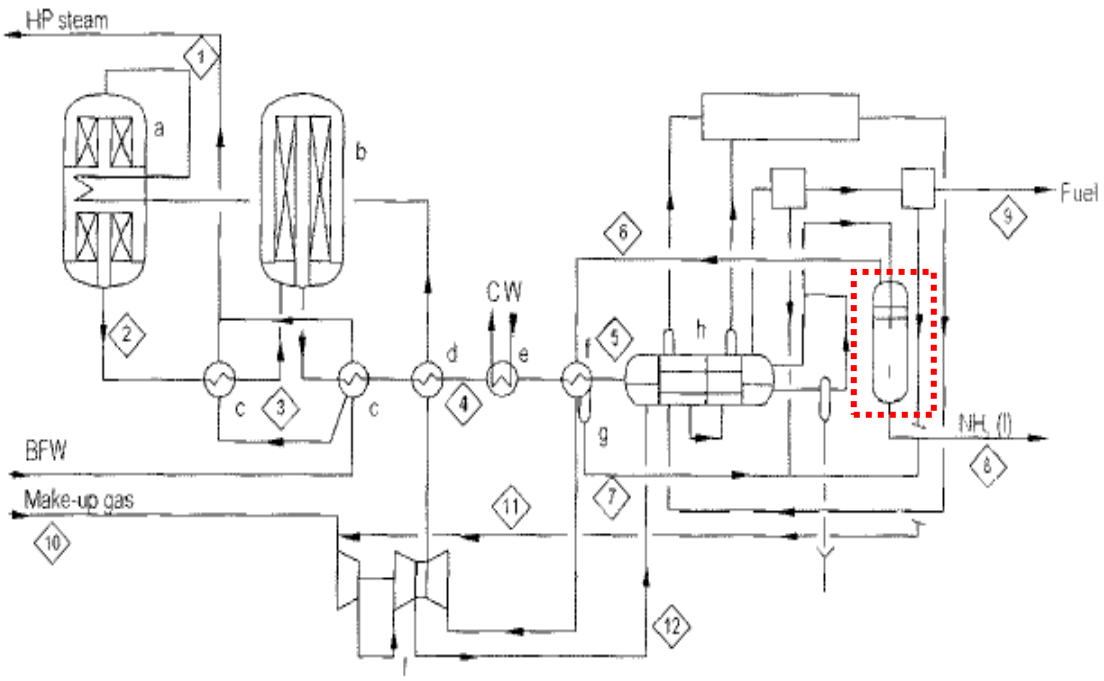


Figure 2.2.2 Modern Ammonia synthesis loop (Krupp – Uhde)

Table 2.2.2 Gas composition from Ammonia synthesis loop (Krupp-Uhde)

No	Flow rate, kmol/h	T, °C	P, MPa	Gas composition, mol %					Production of NH_3 liquid, t/h
				N_2	H_2	CH_4	Ar	NH_3	
1	28344	295	18.80	23.53	61.20	8.20	2.80	4.18	
2	25368	469	18.48	20.43	50.79	9.15	3.23	16.40	
3	25368	401	18.38	20.43	50.79	9.15	3.23	16.40	
4	24672	336	18.26	19.60	47.99	9.43	3.31	19.67	
5	21613	21	18.02	22.33	54.71	10.67	3.78	8.51	
6	28344	0	17.88	23.54	61.20	8.20	2.88	4.18	
7	3060	21	18.02	0.30	0.55	0.50	0.09	98.55	51.36
8	3678	20	2.50	0.002	0.03	0.12	0.01	99.82	62.51
9	320	38	0.25	46.55	21.72	24.34	7.21	0.18	0.01
10	7667	35	3.23	25.89	72.73	1.07	0.31	0.00	
11	374	38	3.25	5.22	90.20	2.86	1.72	0.00	
12	8041	35	18.20	24.93	73.54	1.16	0.37	0.00	

2.2.3 Ammonia Synthesis Loop by Irven Rinard (1999)

Figure 2.2.3 in the next page shows the simplify Ammonia synthesis loop process flow diagram via Haber process explained by Irven Rinard (1999). The Ammonia synthesis reaction is equilibrium limited to the point where it must be run at rather high pressures (200 atm) in order to achieve a reasonable conversion of Syn gas to Ammonia across the Converter. Since the front end of the process is best run at much lower pressures, a Feed Compressor is needed to compress the Syn gas mixture to the operating pressure of the Synthesis Loop.

Due to the unfavorable reaction equilibrium, only part of the Syn gas is converted to Ammonia on a single pass through the Converter. Since the unconverted Syn gas is valuable, the majority of it is recycled back to the Converter. Due to pressure drop through the Synthesis Loop equipment, a Recycle Compressor is required to make up this pressure drop. The recycled Syn gas is mixed with fresh syn gas to provide the feed to the Synthesis Converter.

The effluent from the Synthesis Converter contains product Ammonia as well as unreacted Syn gas. These must be separated. At the pressure of the synthesis loop Ammonia can be condensed at reasonable temperatures. This is done in the Ammonia Condenser where the Syn gas is cooled to approximately ambient temperature using cooling water . The liquid Ammonia is then separated from the cycle gas in the Ammonia Knockout Drum. The liquid Ammonia is removed from the bottom of the drum and the cycle gas leaves the top.

Some of the cycle gas must be purged from the Synthesis Loop. Otherwise, the Argon that enters the loop in the Syn gas has no way to leave and will build up in concentration. This will reduce the rate of the Ammonia synthesis reaction to an unacceptable level. To prevent this from happening, a small amount of the cycle gas must be purged, the amount being determined by the amount of Argon in the feed and its acceptable level in the Synthesis Converter feed (generally about 10 mol %).

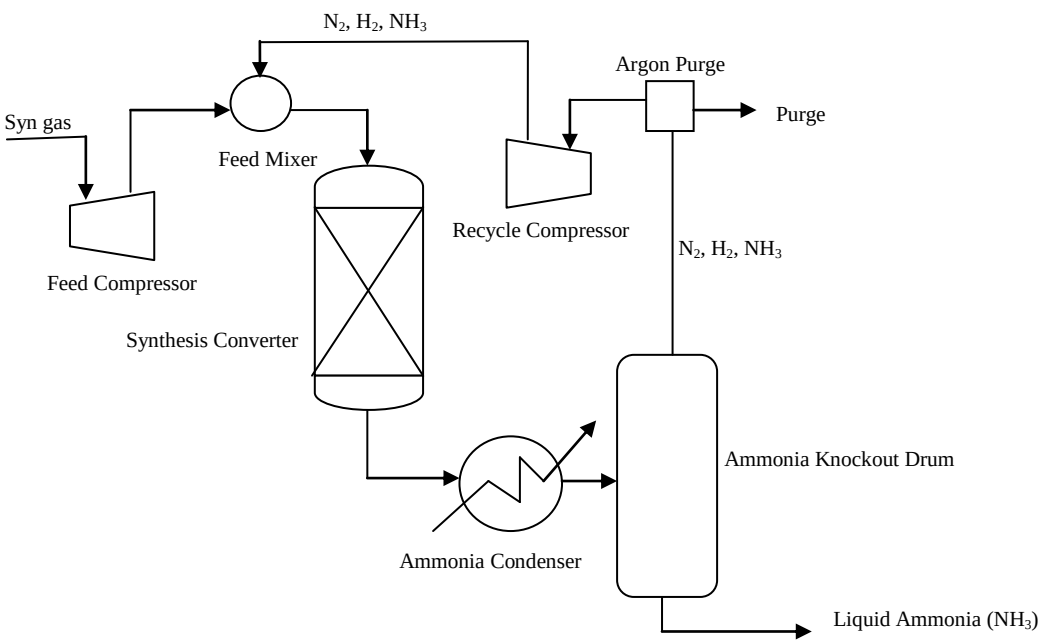


Figure 2.2.3 Ammonia Synthesis Loop Process Flow Diagram (Iren Rinard,1999)

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

Firstly, to address **Objective 1** on to simulate and study the Ammonia synthesis loop using iCON® Process Simulation, model of Ammonia synthesis loop will be simulated in the iCON® software using the current data available of Ammonia synthesis obtained from the literature review. Ammonia synthesis flowsheet can be simulated by iCON® Process Simulation software with a few steps. To draw a flowsheet, a mixture of components should be ensured within the appropriate thermodynamic model to ensure a correct flowsheet is produced.

Meanwhile to address **Objective 2** on investigate the best operating conditions of Ammonia Reactor-Separator System to minimize the fraction of unrecovered Ammonia in the recycled gas. Effect of changing the inlet temperature and pressure of Ammonia Reactor-Separator towards the mol fraction of Ammonia in the recycling stream will be studied. The best operating conditions will be deduced and compared with the literature review.

Figure 3.1(i) below shows the overall process flow diagram for the project throughout Final Year Project period. This is very important in order to make sure the project is going on the correct path.

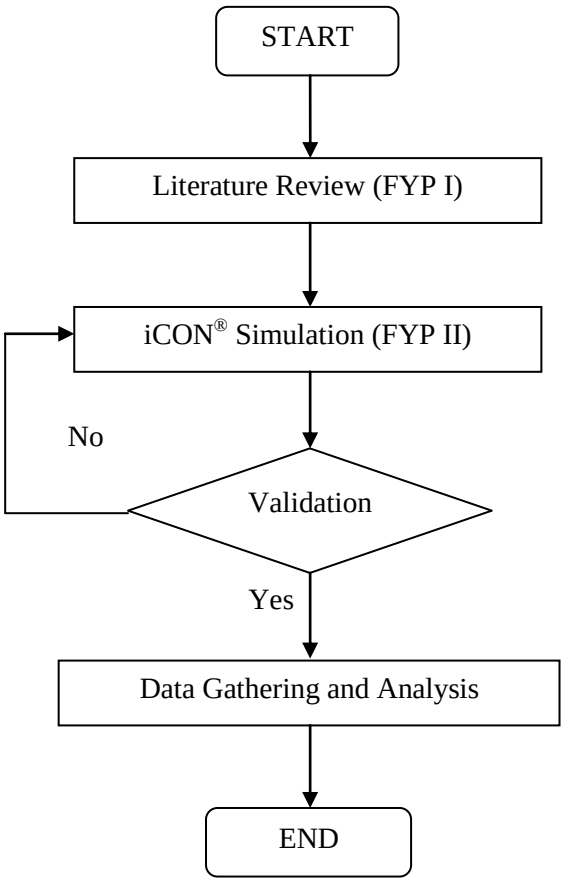


Figure 3.1(i) General Project Flow of Final Year Project

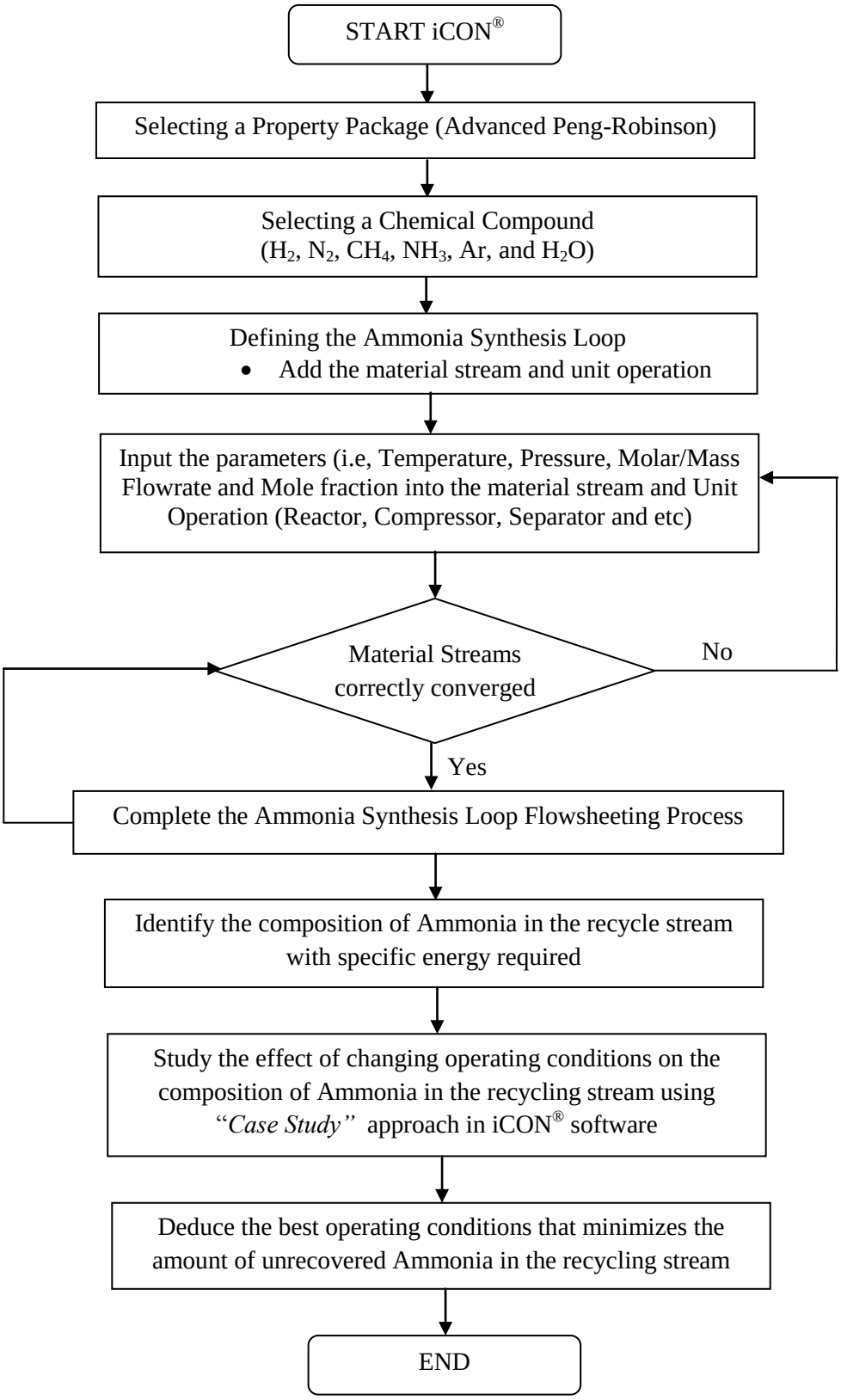
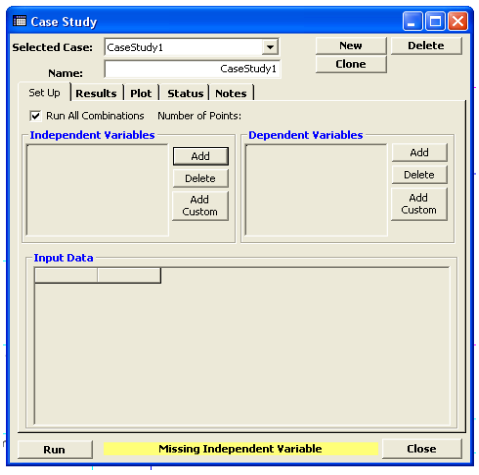


Figure 3.1(ii) iCON® Process Simulation Algorithm

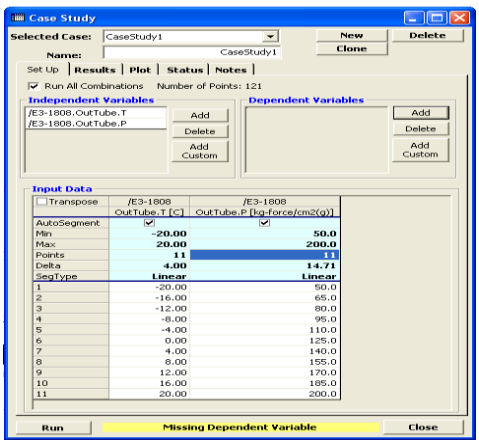
A ‘Case Study’ can be run to see the effect of changing one variable on other variables. Any variable that has been specified can be changed in a case study. **Figure 3.1(iii)** below generalized the step to run the ‘Case Study’ in the iCON®.

Step 1



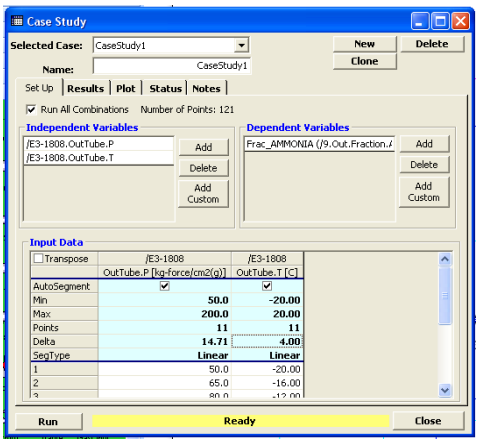
First, open the case study under ‘Tools’. Then, press the ‘Add’ button next to the independent variable frame. Select the independent variable. Here, the independent variable studied is the inlet temperature and pressure of Ammonia Reactor-Separator of Ammonia Synthesis Loop.

Step 2



The range of Temperature and Pressure that will be studied and the number of case study points that will be created need to be specified. The Temperature and Pressure will be studied from -20-20^{o}C and 50-170 kg.f/cm^{2} respectively for Ammonia Separator and 300-500^{o}C and 125-259 kg.f/cm^{2} respectively for Ammonia Reactor.

Step 3



Then, add the dependent variables that will be studied. Here, the dependent variables is the mol fraction of Ammonia in the recycle stream 9. After, all of the variables have been added, pressing ‘Run’ will run the case study to get the necessary values. Once it has been solved, opening the ‘Results’ tab shows the effects of changing the independent variable on the dependent variable that have been specified.

Figure 3.1(iii) Data Analysis using ‘Case Study’ approach in iCON® software

3.2 Project Activities

3.2.1 Final Year Project I (May 2012)

Table 3.2.1 Project Activities for Final Year Project I

Week	Project Activities
2	1st meeting with the Supervisor • Discussed on relevant topics for FYP project
	FYP Topic Chosen: Simulation Study of Ammonia Synthesis Loop Reactor-Separator System – Effect of Reactor-Separator operating condition towards the mol fraction of Ammonia in the recycling stream • Finding relevant information on the topic chosen
3	First Task : • Finding existing Schematic Process Flow Diagram of Ammonia production, How the H_2 and N_2 as raw material are synthesized & relevant operating condition of Ammonia synthesis Loop process
4	Define the Problem Statement, Objective and Scope of the project
5	Study the Ammonia recycling stream in the Ammonia synthesis loop
	Progress with Preliminary extended proposal
6	Submission of Extended Proposal to the Supervisor
7	Defining the Research Methodology of the project
8	Revising the manual of iCON® Process Simulation software for better understanding
9	
10	Interim Oral Presentation with the Supervisor and Internal Examiner
11	Mass Literature Review on various operating conditions of Ammonia synthesis loop from existing experimental work and real plant data.
12	
13	1st Draft Interim Report Submission to the Supervisor
14	Final Draft Interim Report Submission

3.2.2 Final Year Project II (September 2012)

Table 3.2.2 Project Activities for Final Year Project II

Week	Project Activities
1	Exploring iCON® Process Simulation software • Getting to know the iCON® software deeply by doing the tutorial lesson available
2	
3	Study the real plant Ammonia Synthesis loop PFD which emphasise on the amount of unrecoved Ammonia in the recycling stream
4	Simulation using iCON® software at UTP CBT Room (05-02-12) • Input the data in the iCON® software. Run the simulation to check whether the simulation is correctly converged or not
5	
6	
7	
8	Submission of Progress Report to the Supervisor
9	Data Gathering and Analysis • Study the effect of operating condition of Ammonia Reactor-Separator Systems towards the amount of Ammonia in the recycling stream using *'Case Study'* approach in the iCON® software
10	
11	Poster Oral Presentation (Pre-Sedex)
12	Submission of the Draft report Dissertation to the Supervisor
	Final Conclusion and future Recommendation of the project
13	Submission of Softbound Project Dissertation and Technical Report
14	Viva (Final Oral Presentation)
17	Submission of Hardbound Project Dissertation

3.3 Gantt Chart and Key Milestone

Gantt chart with the Key Milestone are prepared in order to effectively organized the timeline of the Final Year Project.

3.3.1 Final Year Project I (May 2012)

Table 3.3.1 Gantt Chart and Key Milestone for Final Year Project I

Semester	**Final Year Project I, Semester 1 (May 2012)**													
Period (Week)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Preliminary Research Work • Literature review on the Ammonia synthesis loop • To study the recycle stream of Ammonia synthesis loop	■	■	■	■	■									
Submission of Extended Proposal						●								
Defining the research methodology of the project							■	■	■					
Interim Oral Presentation										●				
Preliminary conclusion and future project recommendation											■	■	■	
Submission of Draft Interim Report													●	
Submission of Interim Report (Softbound)														●

3.3.2 Final Year Project II (September 2012)

Table 3.3.2 Gantt Chart and Key Milestone for Final Year Project II

Semester	**Final Year Project II, Semester 2 (September 2012)**														
Period (Week)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	17
Synthesis and development of the flowsheet of the Ammonia Synthesis Loop using iCON® Process Simulation Software (**Target**: Simulation correctly converged)	■	■	■	■	■	■	■								
Submission of Progress Report								●							
Study the effect of Temperature and Pressure (Independent Variable) of Reactor-Separator towards the Ammonia mol fraction in the recycling stream using '*case study'* approach via iCON® Process Simulation									■	■					
Pre-Sedex (Poster Presentation)											●				
Work project continuition (Data Gathering and Analysis)											■	■			
Submission of Draft Report Dissertation												●			
Project Report Review and Modification												■	■		
Submission of Dissertation (Softbound)													●		
Submission of Technical Report													●		
Viva (Final Oral Presentation)														●	
Submission of Project Dissertation (Hardnound)															●

3.4 Software

As this project mainly relates about simulation, the project work will use iCON® Proces Simulation software developed by PETRONAS and Virtual Materials Group (VMG) Incorporation that using SIM42 Open-Source simulation frame.

Table 3.4 System Characteristics and Requirements of the Software

Software Model	iCON® Process Simulation software Version 6.5
Developer	Virtual Materials Group, Inc & PETRONAS Group Technology Solutions
Minimum System Requirements	
Minimun Software requirements	Windows 2000 (SP4)/Windows XP(32-bit)/Windows Vista (32 bits) Microsoft Visio Standard Edition 2003 Microsoft Excel 2003 (Recommended to use Excel 2007) Microsoft Word 2003 (Recommended to use Word 2007)
Minimum Hardware Requirement	Pentium IV @ 1.8GHz/Dual Core @ 1.67 GHz 512 MB RAM (1 GB for Windows Vista) Monitor resolution 1920 x 1080
	

(Reference: iCONBasic.pdf, 2003-2011)

From a certain point of view, iCON® is a very sophiscated chemical calculator that uses thermodynamic models to power its Gibbs free energy calculations (and therefore phase equilibrium) and Gibbs phase rule to determine available degrees of freedom for different unit operations and the flow sheet. Selection of the correct thermodynamic models for different process is very important to ensure the accuracy of the calculations.

CHAPTER 4
RESULT AND DISCUSSION

The simulation model for Ammonia Synthesis loop unit was validated using rigorous process simulations carried out in iCON® Process Simulation software v6.5, using Advanced Peng-Robinson as the fluid package.

4.1 iCON® Process Simulation of Ammonia Synthesis Loop

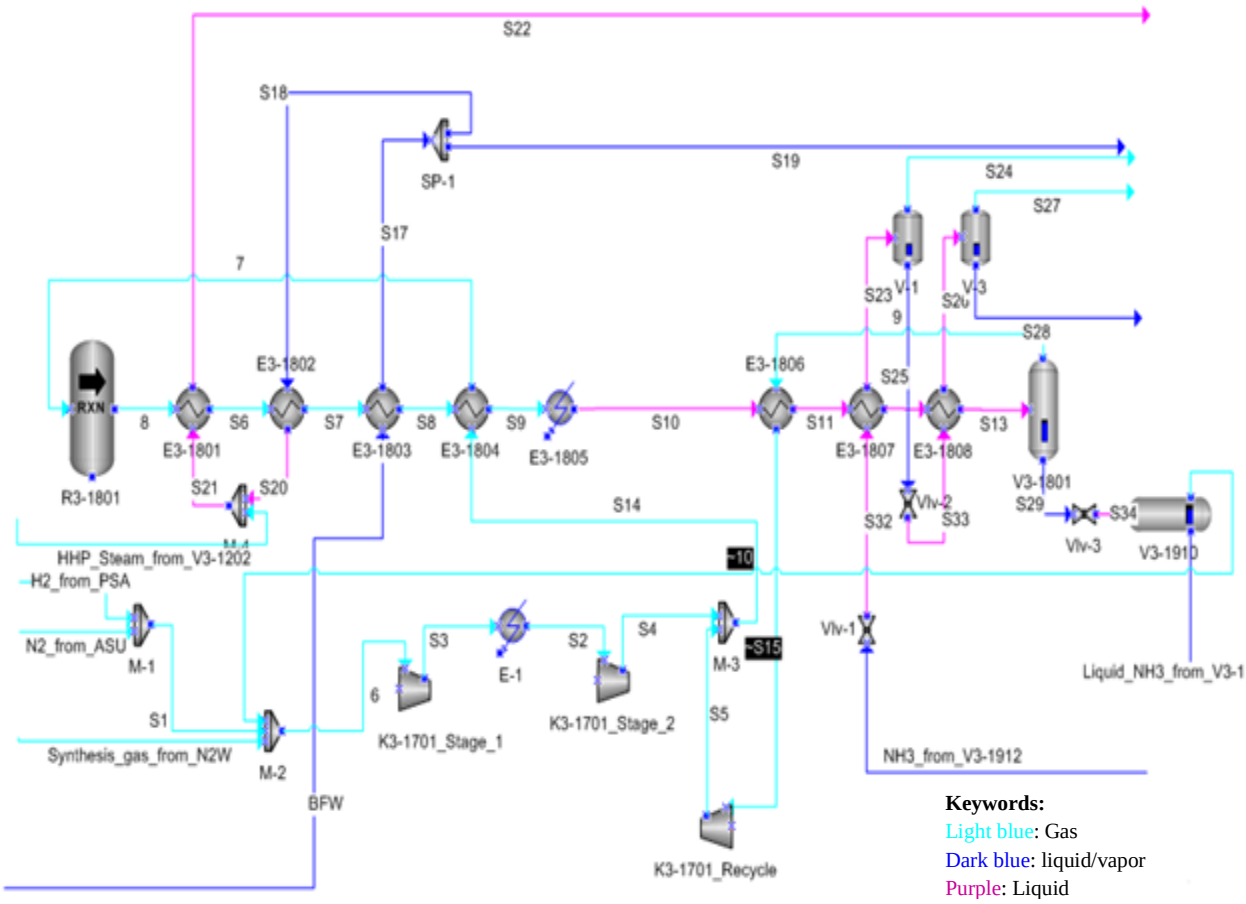


Figure 4.1 Simulation of Ammonia Synthesis loop using iCON® software

4.1.1 Process Description

The Ammonia synthesis loop was modelled using iCON® Process Simulation software. The simulated flowsheet of Ammonia Synthesis loop is shown in **Figure 4.1** above. Synthesis H_2 and N_2 is mixed via M1 Mixer then combined with 75% mol fraction of H_2 and 25% mol fraction of N_2 from the synthesis gas together with recycle stream (S10_1) and fed to the Stage 1 Compresser with efficiency of 0.9. Then, the gas is cooled via Cooler (E-1) with 0.05 bar of pressure drop (ΔP). The mixed gas is fed to another Stage 2 Compresser (η=0.8) before added up with another recycle stream (S5) and the gases is heated via heat exchanger (E3-1804).

The mixed gas that contains 71% mol fraction of H_2 and 24% mol fraction of N_2, is fed to the Ammonia Reactor (R3-1801). The reaction temperature of the Reactor is 456 ^oC and the pressure is 137 kg.force/cm^2. Under these conditions 25% of the Hydrogen and Nitrogen are converted to Ammonia. The product of the reactor produced 0.60315 mol H_2, 0.20533 mol N_2, and 0.19034 mol of NH_3. The gas mixture is now cooled, compressed and fed into the Ammonia Separator. The outlet gas from the Ammonia Reactor is cooled from 456^oC to -1^oC via 5 Heat Exchanger, 1 cooler with 0.05 bar of pressure drop (ΔP) and 2 chillers. Ammonia is used as refrigerating agent in the chillers. This cooling process condenses more the half the Ammonia, which is then separated out.

The top product of Ammonia Separator (V3-1801) consist of 0.06492 mol of unrecovered Ammonia where it is recycled back to the Ammonia Reactor via Stage 3 Ammonia synthesis recycle Compressor (η=0.8). Meanwhile 0.99317 mol of Ammonia at the bottom is further separated via Ammonia Let Down Vessel (V3-1910) which produce 0.99879 mol of Ammonia at the bottom and about 0.19034 mol of Ammonia in the top is recycled and mixed with the synthesis gas in the earlier process.

4.1.2 iCON® simulation of Ammonia Reactor (R3-1801)

Gas Inlet:

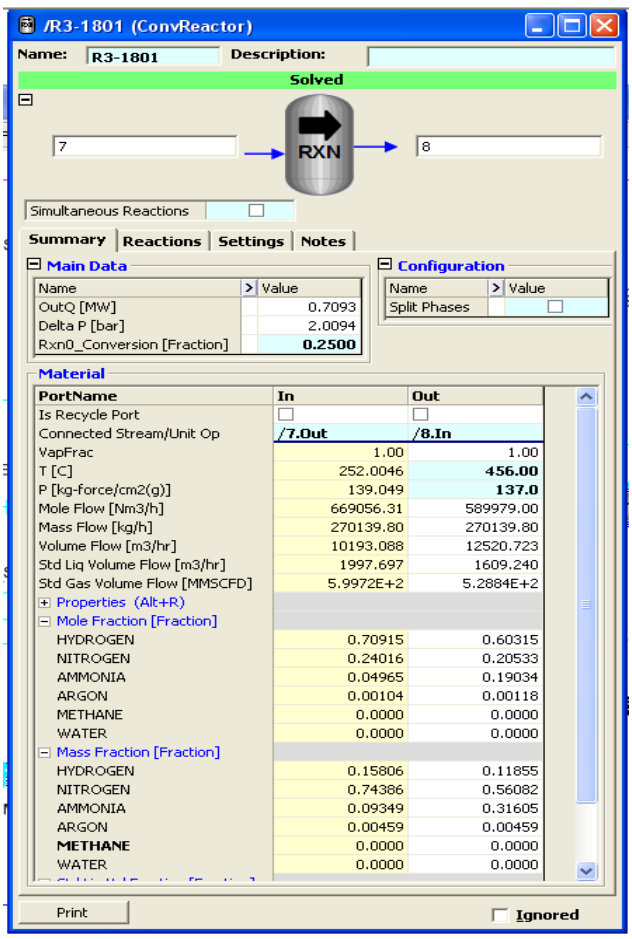
T (°C)	252.0
P (kg.force/cm^2)	139.0
Mol Flow Rate (N m^3/h)	669,056.31
Mole fraction of Ammonia	0.04965

7 → RXN → 8

Gas Outlet:

T (°C)	456.0
P (kg.force/cm^2)	137.0
Mol Flow Rate (N m^3/h)	589,979.0
Mole fraction of Ammonia	0.19034

1 kg.f/cm^2 = 0.967841105 atm



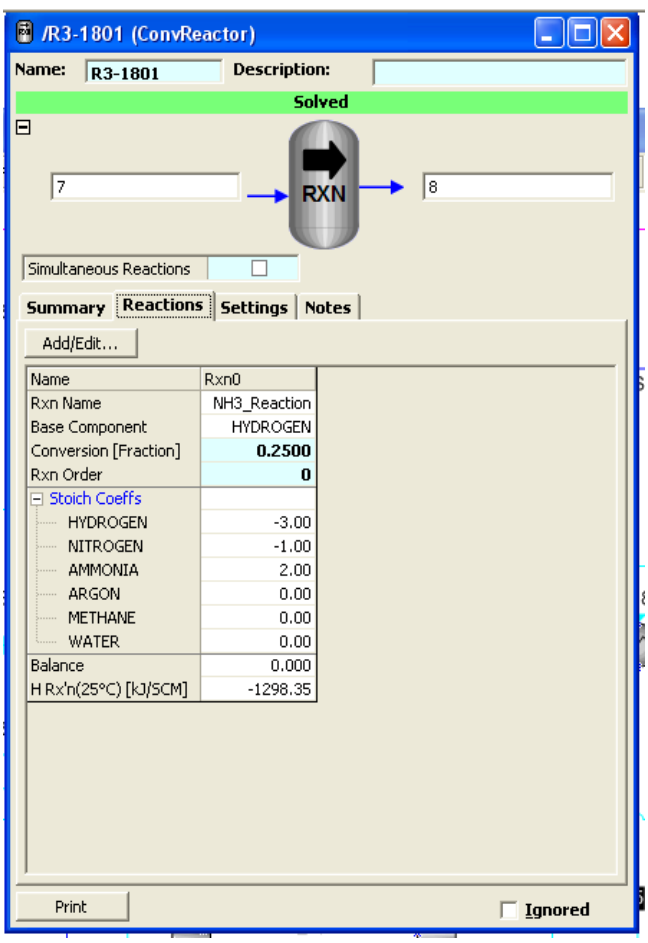


Figure 4.1.2 iCON® simulation of Ammonia Reactor (R3-1801)

Figure 4.1.2 above shows the simulated Ammonia Reactor in the iCON® software where 25% conversion of the Ammonia is specified. The stoichiometry coefficients of the Ammonia reaction also is specified for the simulation of Ammonia Reactor to correctly converged.

4.1.3 iCON® simulation of Ammonia Separator (V3-1801)

Gas Outlet (Top):

T (^oC)	-1.0
P (kg.force/cm^2)	131.0
Mol Flow Rate (N m^3/h)	510,265.25
Mole fraction of Ammonia	0.06492

Liquid Inlet:

Vapor Fraction	0.8649
T (^oC)	-1.0
P (kg.force/cm^2)	131.0
Mol Flow Rate (N m^3/h)	589,979.0
Mole fraction of Ammonia	0.17243

Liquid Outlet (Bottom):

T (^oC)	-1.0
P (kg.force/cm^2)	131.0
Mol Flow Rate (N m^3/h)	79,713.75
Mole fraction of Ammonia	0.99317

1 kg.f/cm^2 = 0.967841105 atm

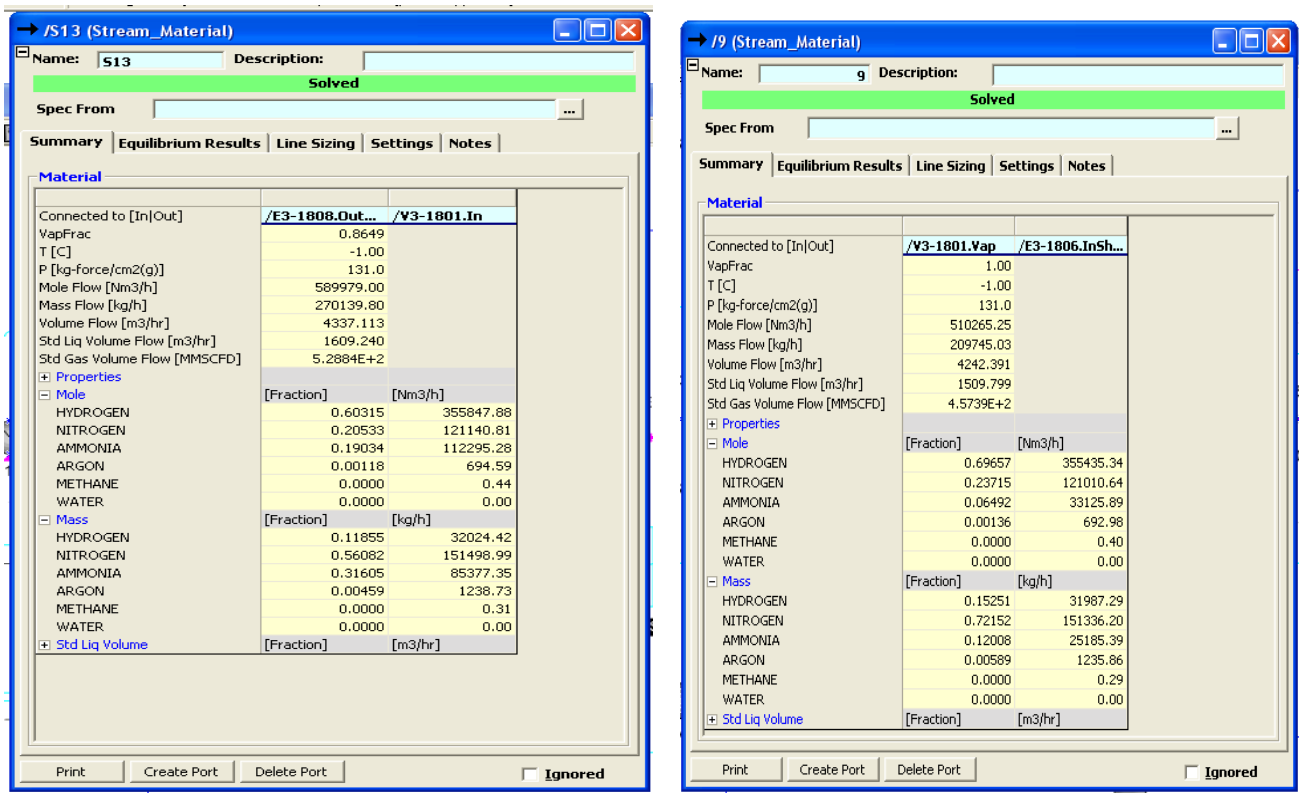


Figure 4.1.3 iCON® simulation of Ammonia Separator (V3-1801)

4.2 Data Gathering and Analysis

Table 4.2(i) Unit operation of Ammonia Synthesis Loop

Unit Operation	Unit(s)	Unit Operation	Unit(s)
Heat Exchanger	4	Ammonia Separator	1
Cooler (Utility)	2	Ammonia Letdown Vessel	1
Chillers	2	Ammonia Reactor	1
Mixer	4	Spiltter	1
Compressor	3		

Table 4.2(ii) Error Analysis

Stream Name	S4			7 (inlet stream of Ammonia Reactor)			8 (outlet stream of Ammonia Reactor)			9 (Recycle stream)		
Composition	Mol Fraction		%	Mol Fraction		%	Mol Fraction		%	Mol Fraction		%
	iCON®	Literature	deviation	iCON®	Literature	deviation	iCON®	Literature	deviation	iCON®	Literature	deviation
Hydrogen	0.7494	0.7498	0.0533	0.7092	0.7105	0.1830	0.6032	0.6061	0.4785	0.6966	0.6986	0.2863
Nitrogen	0.2500	0.2501	0.0400	0.2402	0.2368	1.4358	0.2053	0.2020	1.6337	0.2372	0.2328	1.8900
Ammonia	0.0000	0.000	0.0000	0.0497	0.0455	9.2308	0.1903	0.1897	0.3163	0.0650	0.0592	9.7973
Argon	0.0000	0.0000	0.0000	0.0010	0.0011	9.0909	0.0012	0.0013	7.6923	0.0014	0.0015	6.6667
Methane	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

4.2.1 Effect of inlet Temperature and Pressure of Ammonia Reactor on the Mol Fraction of Ammonia in the recycled gas

Table 4.2.1 Tabulated data of the effect of inlet Temp. and Pressure of Ammonia Reactor towards the $(x_{NH_3})_{recycle}$

T (^oC)	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$
300	125.0	0.0649	138.4	0.0649	151.8	0.0649	165.2	0.0649	178.6	0.0649
320		0.0649		0.0649		0.0649		0.0649		0.0649
340		0.0649		0.0649		0.0649		0.0649		0.0649
360		0.0649		0.0649		0.0649		0.0649		0.0649
380		0.0649		0.0649		0.0649		0.0649		0.0649
400		0.0649		0.0649		0.0649		0.0649		0.0649
420		0.0649		0.0649		0.0649		0.0649		0.0649
440		0.0649		0.0649		0.0649		0.0649		0.0649
460		0.0649		0.0649		0.0649		0.0649		0.0649
480		0.0649		0.0649		0.0649		0.0649		0.0649
500		0.0649		0.0649		0.0649		0.0649		0.0649

T (^oC)	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$
300	192.0	0.0649	205.4	0.0649	218.8	0.0649	232.2	0.0649	245.6	0.0649	259.0	0.0649
320		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
340		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
360		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
380		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
400		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
420		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
440		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
460		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
480		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649
500		0.0649		0.0649		0.0649		0.0649		0.0649		0.0649

1 $kg.f/cm^2$ = 0.967841105 atm

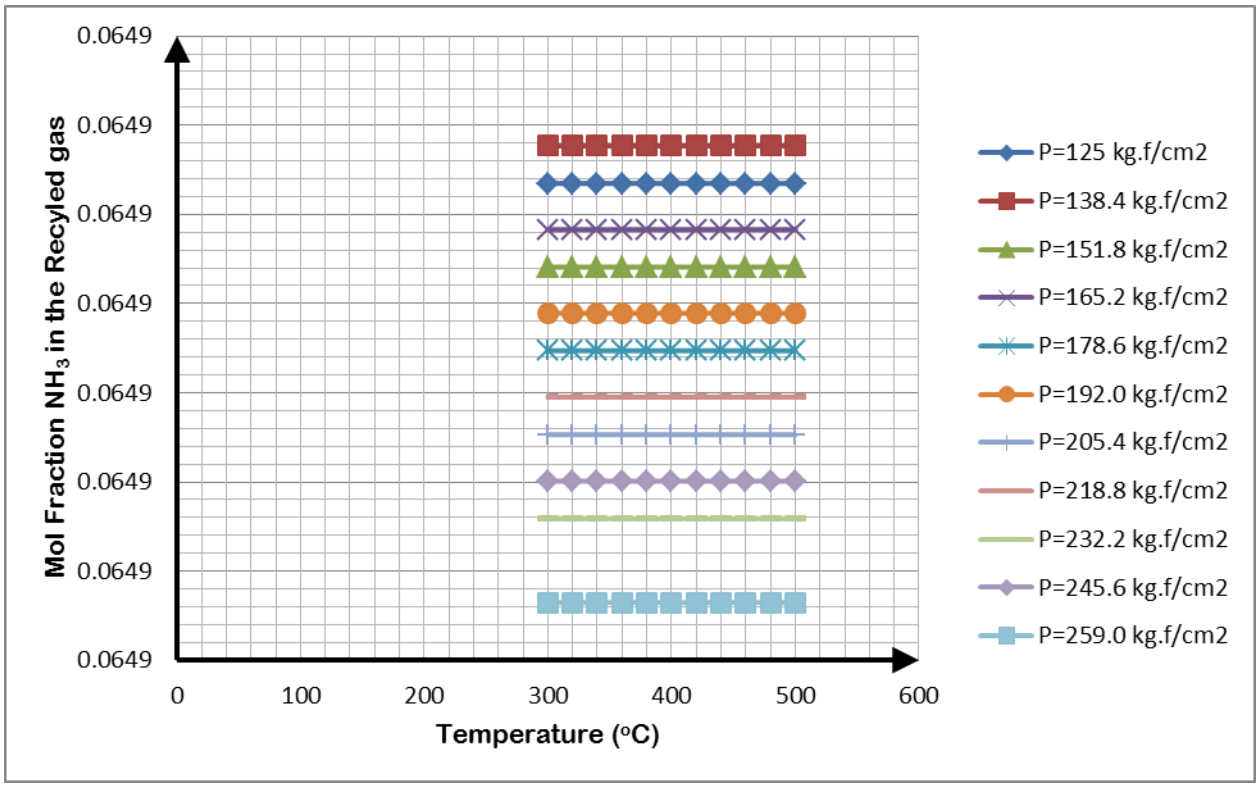


Figure 4.2.1 Graph of Mol Fraction of Ammonia in the recycled gas vs. inlet Temperature and Pressure of Ammonia Reactor

Figure 4.2.1 above shows the iCON® simulation analysis on the effect of inlet temperature ranging from 300-500 ^{o}C and inlet pressure between 125-259 kg.f/cm^2 of Ammonia Reactor on the composition of Ammonia in the recycled gas. From the plot, it shows that the composition of Ammonia in the recycled gas is constant throughout the temperature and pressure range studied. One of the reasons because, the kinetic constant is not incorporated in the Ammonia Reactor simulation. Based on the Arrhenius equation, it relates the rate constant of a chemical reaction to the exponential value of the temperature.

$$k_n = A \exp\left(\frac{-E}{RT}\right)$$

where; A is the pre-exponential factor

E is the activation energy

R is the rate constant and

T is its temperature.

For most of the reactions, temperature has a marked effect on the rate of reaction. In general, the rate of reaction increases with increasing the temperature.

4.2.2 Effect of inlet Temperature and Pressure of Ammonia Separator on the Mol Fraction of Ammonia in the recycled gas

Table 4.2.2 Tabulated data of the effect of inlet Temp. and Pressure of Ammonia Separator towards the $(x_{NH_3})_{recycle}$

T (^oC)	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$
-20.0	50.0	0.0543	65.0	0.0459	80.0	0.0408	95.0	0.0375	110.0	0.0351
-16.0		0.0639		0.0540		0.0479		0.0438		0.0410
-12.0		0.0748		0.0631		0.0558		0.0510		0.0477
-8.0		0.0871		0.0733		0.0648		0.0591		0.0551
-4.0		0.1008		0.0847		0.0747		0.0681		0.0634
0.0		0.1162		0.0974		0.0858		0.0780		0.0726
4.0		0.1332		0.1115		0.0981		0.0891		0.0827
8.0		0.1520		0.1271		0.1116		0.1012		0.0939
12.0		0.1727		0.1442		0.1265		0.1146		0.1061
16.0		0.1954		0.1629		0.1427		0.1291		0.1194
20.0		0.2202		0.1834		0.1605		0.1450		0.1340

T (^oC)	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$	P ($kg.f/cm^2$)	Mol Fraction, $(x_{NH_3})_{recycle}$
-20.0	125.0	0.0335	140.0	0.0323	155.0	0.0314	170.0	0.0309
-16.0		0.0390		0.0376		0.0365		0.0358
-12.0		0.0453		0.0435		0.0422		0.0413
-8.0		0.0522		0.0501		0.0486		0.0474
-4.0		0.0600		0.0575		0.0556		0.0542
0.0		0.0686		0.0656		0.0634		0.0617
4.0		0.0780		0.0746		0.0719		0.0699
8.0		0.0884		0.0844		0.0813		0.0789
12.0		0.0999		0.0952		0.0916		0.0888
16.0		0.1123		0.1069		0.1027		0.0995
20.0		0.1258		0.1196		0.1149		0.1112

1 $kg.f/cm^2$ = 0.967841105 atm

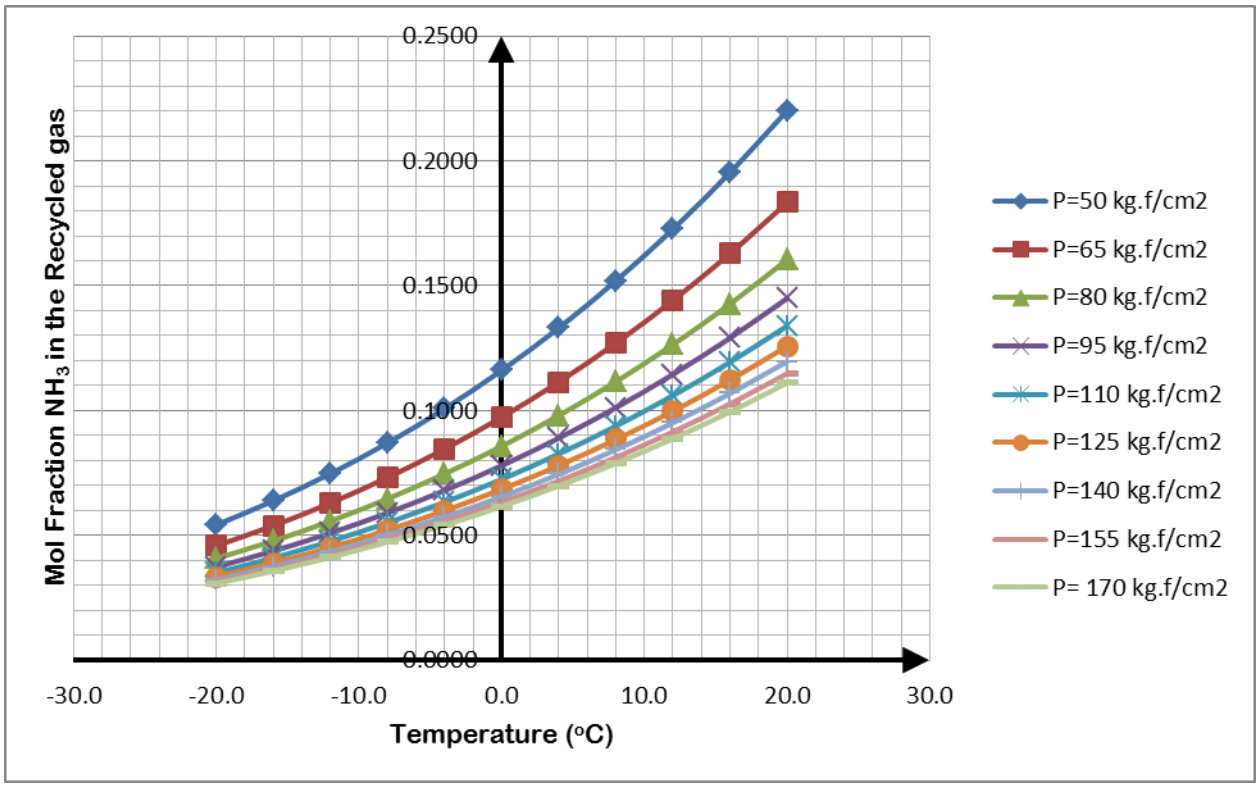


Figure 4.2.2 Graph of Mol Fraction of Ammonia in the recycled gas vs. inlet Temperature and Pressure of Ammonia Separator

Figure 4.2.2 above shows iCON® simulation analysis on the effect of inlet temperature ranging from -20-20°C and inlet pressure ranging from 50-170 kg.f/cm^2 of the Ammonia Separator on the composition of Ammonia in the recycled gas. From the plot, it shows that the composition of Ammonia in the recycled gas is decreasing as the temperature decreased and as the pressure increased. Thus, from the analysis of graph, the best operating inlet temperature and pressure of Ammonia Separator is -5.0 °C and 140 kg.f/cm^2 respectively. These values have been deduced as it is reflective to same values reported by the literature review of Ammonia Synthesis Loop process.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

As a conclusion, the prediction model of Ammonia Synthesis Loop is successfully performed using iCON® Process Simulation software. From the simulation, some results obtained show good agreement and follow trends in referred literatures. It can be concluded that at at low temperature and high pressure in the inlet stream of Ammonia separator, the percent of unrecovered Ammonia is reduced in the recycling stream. It is deduced that, the best inlet temperature and pressure of Ammonia Separator is -5.0 ^{o}C and 140 kg.f/cm^{2} respectively. Where, at this temperature and pressure, the amount of Ammonia in the recycled gas is about 0.05 mol fraction as reported by the literature review. Meanwhile, the analysis of graph shows that the amount of unrecovered Amonia in the recycling stream is constant when the inlet temperature and pressure of the Ammonia Reactor were varied. The most probably reason is because, the reaction kinetics of the Reactor is not specified in the Reactor.

Hence, as a recommendation, methods of flowsheet development for Ammonia synthesis loop using iCON® Process Simulation software need to be constructed precisely using correct thermodynamic property to increase the quality of the results. Single unit of reactor, separator, heat exchanger and others equipment in simulation can be developed to be more presentable to the actual physical equipment which already existed. It also recommended that experiments can be conducted to generate more valuable reaction kinetics that will give higher impact on the simulation work. Exact chemical formula of Ammonia synthesis should be used to reflect the experimental conditions and subsequently improve simulation results.

Also, based on the foregoing discussion and the evaluation of present technology and research efforts, one may formulate the scenario for the future development of Ammonia production. It is recommended that from newer technology developements of Ammonia production, the primary concern is to reduce investment costs on the energy required to run Ammonia plant but in the same time increase the operational reliability. For example, smaller integrated process units, such as reactor and separator in various configurations, contribute to this reduction and will achieve

additional energy consumption savings by reducing the composition of unrecovered Ammonia and subsequently produce high yield of Ammonia. But, again progress in experimental and simulation control could reduce the overall energy consumption by tuning the Ammonia plants continuously to optimal operating conditions and generating high profit.

In addition, the range of operating conditions involve Capital-Energy Trade-Offs as shown in **Figure 5.0** below. For instance, higher pressure can increase the equilibrium conversions but in the same time will increase the cost of compressing the reaction gases. Meanwhile lower the reactor temperature will increase equilibrium conversion but increase cost by requiring more cooling to remove heat from the exothermic reaction. Another example is, smaller purge-to-recycle ratios loose less reaction gas from the recycle loop but increase cost since more gas must be compressed for recycle back to the reactor.

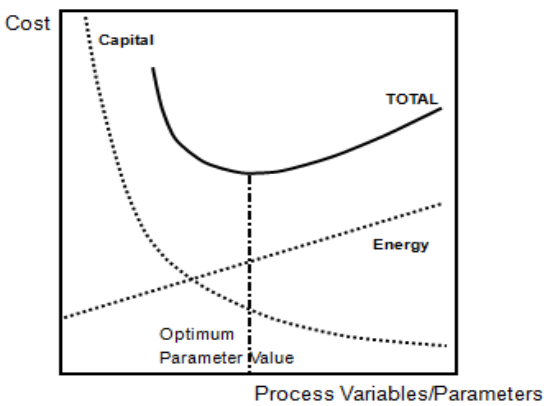


Figure 5.0 The Capital-Energy Trade-Offs

Hence, the capital trade off effect in setting the operating parameter have to be considered. By simulating using iCON® process simulation software, the temperature, concentrations and pressure profiles of Ammonia synthesis reactor and separator will be obtained and the corellation will be developed to find the best operating conditions in minimizing the percent of unrecovered Ammonia in the recycled gas.

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APPENDIX

Table A1. Streams Summary of Ammonia Synthesis Loop from iCON®

Name	6		7		8		9		10	
Upstream Op	M-2.Out		E3-1804.OutShell		R3-1801.Out		V3-1801.Vap		V3-1910.Vap	
Downstream Op	K3-1701_Stage_1.In		R3-1801.In		E3-1801.InTube		E3-1806.InShell		M-2.In2	
VapFrac	1.00		1.00		1.00		1.00		1.00	
T [C]	36.5555		252.0046		456.00		-1.00		1.1802	
P [kg-force/cm2(g)]	29.3		139.049		137.0		131.0		31.0	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.74941	119011.33	0.70915	474463.84	0.60315	355847.88	0.69657	355435.34	0.63007	341.79
NITROGEN	0.24991	39687.21	0.24016	160679.46	0.20533	121140.81	0.23715	121010.64	0.1955	106.05
AMMONIA	0.00059	93.58	0.04965	33217.98	0.19034	112295.28	0.06492	33125.89	0.17251	93.58
ARGON	0.0001	15.35	0.00104	694.59	0.00118	694.59	0.00136	692.98	0.00192	1.04
METHANE	0.0000	0.00	0.0000	0.44	0.0000	0.44	0.0000	0.40	0.0000	0.00
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	158807.47	1.0000	669056.31	1.00	589979.00	1.00	510265.25	1.00	542.47
Mass Flow [kg/h]	60441.83		270139.80		270139.80		209745.03		236.40	
Energy [MW]	17.0319		126.8575		165.0006		46.5157		0.0515	

Name	BFW		H2_from_PSA		HHP_Steam_from_V3-1202		Liquid_NH3_from_V3-1910		N2_from_ASU	
Upstream Op							V3-1910.Liq0			
Downstream Op	E3-1803.InShell		M-1.In1		M-4.In0				M-1.In0	
VapFrac	0.00		1.00		1.00		0.00		1.00	
T [C]	124.00		39.00		324.00		1.1801		33.00	
P [kg-force/cm2(g)]	130.0		29.3		120.0		31.0		32.0	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.0000	0.00	1.0000	45804.00	0.0000	0.00	0.00089	70.80	0.0000	0.00
NITROGEN	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0003	24.11	0.9997	15289.41
AMMONIA	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.99879	79075.82	0.0000	0.00
ARGON	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00001	0.55	0.0003	4.59
METHANE	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.03	0.0000	0.00
WATER	1.0000	91268.43	0.0000	0.00	1.0000	166897.53	0.0000	0.00	0.0000	0.00
Total	1.00	91268.43	1.00	45804.00	1.00	166897.53	1.00	79171.30	1.00	15294.00
Mass Flow [kg/h]	73403.00		4122.12		134228.00		60158.34		19129.16	
Energy [MW]	-29.9505		4.8891		30.4237		-12.6185		1.6556	

Name	NH3_from_V3-1912		S1		S2		S3		S4	
Upstream Op			M-1.Out		E-1.Out		K3-1701_Stage_1.Out		K3-1701_Stage_2.Out	
Downstream Op	Vlv-1.In		M-2.In1		K3-1701_Stage_2.In		E-1.In		M-3.In1	
VapFrac	0.00		1.00		1.00		1.00		1.00	
T [C]	40.00		36.2147		32.00		149.7046		109.4364	
P [kg-force/cm2(g)]	14.769		29.3		72.949		73.0		139.1	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.0000	0.00	0.74968	45804.00	0.74941	119011.33	0.74941	119011.33	0.74941	119011.33
NITROGEN	0.0000	0.00	0.25024	15289.41	0.24991	39687.21	0.24991	39687.21	0.24991	39687.21
AMMONIA	1.0000	88004.20	0.0000	0.00	0.00059	93.58	0.00059	93.58	0.00059	93.58
ARGON	0.0000	0.00	0.00008	4.59	0.0001	15.35	0.0001	15.35	0.0001	15.35
METHANE	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	88004.20	1.00	61098.00	1.00	158807.47	1.00	158807.47	1.00	158807.47
Mass Flow [kg/h]	66909.00		23251.27		60441.83		60441.83		60441.83	
Energy [MW]	-10.6232		6.5447		16.7913		23.6591		21.4405	

Name	S5		S6		S7		S8		S9	
Upstream Op	K3-1701_Recycle.Out		E3-1801.OutTube		E3-1802.OutTube		E3-1803.OutTube		E3-1804.OutTube	
Downstream Op	M-3.In0		E3-1802.InTube		E3-1803.InTube		E3-1804.InTube		E3-1805.In	
VapFrac	1.00		1.00		1.00		1.00		1.00	
T [C]	35.995		408.00		335.00		293.00		87.00	
P [kg-force/cm2(g)]	139.1		136.949		136.898		136.847		136.796	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.69663	355452.51	0.60315	355847.88	0.60315	355847.88	0.60315	355847.88	0.60315	355847.88
NITROGEN	0.23712	120992.25	0.20533	121140.81	0.20533	121140.81	0.20533	121140.81	0.20533	121140.81
AMMONIA	0.06492	33124.39	0.19034	112295.28	0.19034	112295.28	0.19034	112295.28	0.19034	112295.28
ARGON	0.00133	679.24	0.00118	694.59	0.00118	694.59	0.00118	694.59	0.00118	694.59
METHANE	0.0000	0.43	0.0000	0.44	0.0000	0.44	0.0000	0.44	0.0000	0.44
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	510248.83	1.00	589979.00	1.00	589979.00	1.00	589979.00	1.00	589979.00
Mass Flow [kg/h]	209697.97		270139.80		270139.80		270139.80		270139.80	
Energy [MW]	54.0449		152.9738		134.8167		124.4209		73.0488	

Name	S10		S11		S12		S13		S14	
Upstream Op	E3-1805.Out		E3-1806.OutTube		E3-1807.OutTube		E3-1808.OutTube		M-3.Out	
Downstream Op	E3-1806.InTube		E3-1807.InTube		E3-1808.InTube		V3-1801.In		E3-1804.InShell	
VapFrac	0.9805		0.943		0.9003		0.8649		1.00	
T [C]	34.00		26.00		14.00		-1.00		52.4174	
P [kg-force/cm2(g)]	136.745		136.694		136.643		131.0		139.1	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.60315	355847.88	0.60315	355847.88	0.60315	355847.88	0.60315	355847.88	0.70915	474463.84
NITROGEN	0.20533	121140.81	0.20533	121140.81	0.20533	121140.81	0.20533	121140.81	0.24016	160679.46
AMMONIA	0.19034	112295.28	0.19034	112295.28	0.19034	112295.28	0.19034	112295.28	0.04965	33217.98
ARGON	0.00118	694.59	0.00118	694.59	0.00118	694.59	0.00118	694.59	0.00104	694.59
METHANE	0.0000	0.44	0.0000	0.44	0.0000	0.44	0.0000	0.44	0.0000	0.44
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	589979.00	1.00	589979.00	1.00	589979.00	1.00	589979.00	1.0000	669056.31
Mass Flow [kg/h]	270139.80		270139.80		270139.80		270139.80		270139.80	
Energy [MW]	57.0287		50.6414		42.3788		33.9486		75.4854	

Name	S15		S17		S18		S19		S20	
Upstream Op	E3-1806.OutShell		E3-1803.OutShell		SP-1.Out1		SP-1.Out0		E3-1802.OutShell	
Downstream Op	K3-1701_Recycle.In		SP-1.In		E3-1802.InShell				M-4.In1	
VapFrac	1.00		0.00		0.00		0.00		0.2695	
T [C]	30.1206		238.8352		238.8352		238.8352		329.3825	
P [kg-force/cm2(g)]	130.949		129.949		129.949		129.949		129.898	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.69663	355452.51	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
NITROGEN	0.23712	120992.25	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
AMMONIA	0.06492	33124.39	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
ARGON	0.00133	679.24	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
METHANE	0.0000	0.43	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
WATER	0.0000	0.00	1.0000	91268.43	1.0000	90973.75	1.0000	294.68	1.0000	90973.75
Total	1.00	510248.83	1.00	91268.43	1.00	90973.75	1.00	294.68	1.00	90973.75
Mass Flow [kg/h]	209697.97		73403.00		73166.00		237.00		73166.00	
Energy [MW]	52.902		-19.5547		-19.4916		-0.0631		-1.3344	

Name	S21		S22		S23		S24		S25	
Upstream Op	M-4.Out		E3-1801.OutShell		E3-1807.OutShell		V-1.Vap		V-1.Liq0	
Downstream Op	E3-1801.InShell				V-1.In				Vlv-2.In	
VapFrac	0.7527		0.9202		0.4659		1.00		0.00	
T [C]	323.3348		323.3027		11.7201		11.7201		11.7201	
P [kg-force/cm2(g)]	120.0		119.949		5.6		5.6		5.6	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
NITROGEN	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
AMMONIA	0.0000	0.00	0.0000	0.00	1.0000	88004.20	1.0000	41003.93	1.0000	47000.28
ARGON	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
METHANE	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
WATER	1.0000	257871.27	1.0000	257871.27	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	257871.27	1.00	257871.27	1.00	88004.20	1.00	41003.93	1.00	47000.28
Mass Flow [kg/h]	207394.00		207394.00		66909.00		31175.01		35733.99	
Energy [MW]	29.0892		41.116		-2.3606		4.688		-7.0487	

Name	S26		S27		S28		S29		S32	
Upstream Op	E3-1808.OutShell		V-3.Vap		V-3.Liq0		V3-1801.Liq0		Vlv-1.Out	
Downstream Op	V-3.In						Vlv-3.In		E3-1807.InShell	
VapFrac	0.7084		1.00		0.00		0.00		0.1047	
T [C]	-3.818		-3.818		-3.818		-1.00		13.4542	
P [kg-force/cm2(g)]	2.749		2.749		2.749		131.0		6.0	
Mole Flow/Composition	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h	Fraction	N m³/h
HYDROGEN	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00518	412.54	0.0000	0.00
NITROGEN	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00163	130.17	0.0000	0.00
AMMONIA	1.0000	47000.28	1.0000	33292.76	1.0000	13707.52	0.99317	79169.40	1.0000	88004.20
ARGON	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00002	1.61	0.0000	0.00
METHANE	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.03	0.0000	0.00
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	47000.28	1.00	33292.76	1.00	13707.52	1.00	79713.75	1.00	88004.20
Mass Flow [kg/h]	35733.99		25312.26		10421.73		60394.77		66909.00	
Energy [MW]	1.3816		3.645		-2.2635		-12.5671		-10.6232	

Name	S33		S34		Synthesis_gas_from_N2W	
Upstream Op	Vlv-2.Out		Vlv-3.Out			
Downstream Op	E3-1808.InShell		V3-1910.In		M-2.In0	
VapFrac	0.054		0.0068		1.00	
T [C]	-3.4694		1.1801		37.00	
P [kg-force/cm2(g)]	2.8		31.0		29.5	
Mole Flow/Composition	Fraction	N m^3/h	Fraction	N m^3/h	Fraction	N m^3/h
HYDROGEN	0.0000	0.00	0.00518	412.54	0.7499	72865.53
NITROGEN	0.0000	0.00	0.00163	130.17	0.2500	24291.75
AMMONIA	1.0000	47000.28	0.99317	79169.40	0.0000	0.00
ARGON	0.0000	0.00	0.00002	1.61	0.0001	9.72
METHANE	0.0000	0.00	0.0000	0.03	0.0000	0.00
WATER	0.0000	0.00	0.0000	0.00	0.0000	0.00
Total	1.00	47000.28	1.00	79713.75	1.00	97167.00
Mass Flow [kg/h]	35733.99		60394.77		36954.16	
Energy [MW]	-7.0487		-12.5671		10.4358	